



CFO 5745 US

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# S P E C I F I C A T I O N

TO ALL WHOM IT MAY CONCERN:

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Mizuhiki 2-chome, Atsugi-shi, Kanagawa-ken, Japan and  
2-14-308, Namiki 2-chome, Kanazawa-ku, Yokohama-shi,  
Kanagawa-ken, Japan, have jointly invented a certain new  
25 and useful improvement in ELECTRON-EMITTING DEVICE of  
which the following is a full, clear, concise and exact  
description.



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TITLE OF THE INVENTION

Electron-emitting device

Related Application

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*Ins. a1* ~~This is a continuation-in-part of application  
Serial No. 07/218,203, filed July 13, 1988.~~

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## BACKGROUND OF THE INVENTION

### 5 Field of the Invention

The present invention relates to an electron-emitting device, and a method of preparing it.

### Related Background Art

Hitherto known as a device achievable of  
10 emission of electrons with use of a simple structure is the cold cathode device published by M.I. Elinson et al (Radio Eng. Electron. Phys., Vol. 10, pp.1290-1296, 1965.

This utilizes the phenomenon in which electron  
15 emission is caused by flowing an electric current to a thin film formed with a small area on a substrate and in parallel to the surface of the film, and is generally called a surface conduction electron-emitting device.

20 This surface conduction electron-emitting device that has been reported includes those employing a  $\text{SnO}_2(\text{Sb})$  thin film developed by Elinson et al. named in the above, those employing an Au thin film (G. Dittmer, "Thin Solid Films", Vol. 9, p.317, 1972),  
25 those employing an ITO thin film, (M. Hartwell and C.G. Fonstad, "IEEE Trans. ED Conf.", p.519, 1975),

1 and those employing a carbon thin film [Hisashi Araki,  
et al. "SHINKU" (Vacuum), Vol. 26, No. 1, p.22, 1983].

Typical device constitution of these surface  
conduction electron-emitting devices is shown in Fig.  
5 38. In Fig. 38, the numerals 19 and 20 denote  
electrodes for attaining electrical connection; 21, a  
thin film formed using an electron-emitting material;  
23, a substrate; and 22, an electron-emitting region.

In these surface conduction electron-emitting  
10 devices, it has been hitherto practiced to previously  
form the electron-emitting region by an energizing  
heat treatment, called "forming", before effecting the  
electron emission. More specifically, a voltage is  
applied between the above electrode 19 and electrode  
15 20 to energize the thin film 21 to bring the thin film  
21 to be locally destroyed, deformed or denatured  
owing to the Joule heat thereby generated, thus  
forming the electron-emitting region 22 kept in a  
state of electrically high resistance to obtain an  
20 electron-emitting function.

What is meant by the above state of  
electrically high resistance is a discontinuous state  
of a film partly having cracks of 0.5  $\mu\text{m}$  to 5  $\mu\text{m}$  on  
the thin film 21 and having the so-called island  
25 structure inside the cracks. What is meant by the  
island structure is the structure of a film in which

1 fine particles generally having a diameter of several  
ten angstroms to several micrometers are present on  
the substrate, and the respective fine particles are  
spatially discontinuous and electrically continuous.

5 Hitherto, in the surface conduction  
electron-emitting devices, a voltage is applied to the  
above high-resistance discontinuous film by the  
electrodes 19 and 20 to flow an electric current to  
the surface of the device, so that the electrons are  
10 emitted from the above fine particles.

However, the forming according to the  
conventional energizing heat treatment as mentioned  
above have involved the problems as follows:

(1) In carrying out the energizing heating, it  
15 sometimes occurs that the thin film is peeled because  
of the difference in coefficient of thermal expansion  
between the substrate and the thin film. This  
provides limitations in upper limit of heating  
temperature, materials for the substrate, and  
20 combination by selection of materials for the thin  
film.

(2) In carrying out the energizing heating, the  
substrate also is locally heated, therefore sometimes  
resulting in occurrence of fatal cracking therein.

25 (3) Degree of the changes of a film owing to the  
energizing heating, as exemplified by the degree of

1 local destruction, deformation or denaturing, tends to  
become irregular among a plurality of devices formed  
in the same substrate, and also the site at which  
changes may occur tends to be not fixed.

5 ✓ For this reason, when functioned as an  
electron-emitting device, irregularity in the shape of  
beams of emitted electrons has been seen for each  
device.

(4) A relatively large electric power is required  
10 until the forming is completed. For this reason, an  
electric source of large capacity is required when a  
number of devices are formed on the same substrate and  
the forming is carried out simultaneously.

(5) A relatively long period of time is required  
15 for conventional forming processes that start with the  
energizing heating and end with cooling. For this  
reason, <sup>an excessively</sup> ~~a greatly~~ long time is required for carrying  
out the forming of a number of devices.

3 ✓ Because of the problems as set out above, the  
20 surface conduction electron-emitting devices have not  
been positively applied in industrial fields,  
notwithstanding their advantages that the device has  
simple construction.

25 SUMMARY OF THE INVENTION

The present invention was made to eliminate

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1 the disadvantages in the prior art as discussed above,  
and an object thereof is to provide an electron-  
emitting device that can have, without applying the  
treatment called forming, a quality more than equal to  
5 that of electron-emitting devices obtained by the  
forming, and has a novel structure suffering less  
irregularity of characteristics, and a method for  
preparing it.

More specifically, the present invention  
10 firstly provides a means for preparing the device by  
controlling the above-mentioned shape and width of  
cracks without use of the forming means, and with  
ease, and provides an electron-emitting device with  
regular characteristics, prepared by the method using  
15 the means.

It secondly provides a means for making  
uniform the structure and size corresponding to the  
island structure in the cracks mentioned above, and  
provides an electron-emitting device having regular  
20 characteristics by using the means.

A further object of the present invention is  
to provide an electron-emitting device capable of  
controlling the above characteristics and also capable  
of better controlling the position of the electron-  
25 emitting region, and a method for preparing such a  
device.

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1           A still further object of the present  
invention is to provide an electric current emitting  
device that not only can solve the problems previously  
mentioned, but also can make lower the voltage to be  
5 applied to electrodes and achieve improvement in the  
density of an emitted electric current.

          According to an aspect of the present  
invention, there is provided an electron-emitting  
device comprising a laminate comprising an insulating  
10 layer held between a pair of electrodes opposing each  
other, wherein an electron-emitting region insulated  
from said electrodes is formed at a side end surface  
of the insulating layer formed at the part at which  
the electrodes oppose each other, and electrons are  
15 emitted from said electron-emitting region by applying  
a voltage between said electrodes.

          According to another aspect of the present  
invention, there is provided an electron-emitting  
device comprising a device structure in which an  
20 insulating layer is formed between opposing electrodes  
, and fine particles are arranged inside the layer of  
said insulating layer in a dispersed state.

          According to a further aspect of the present  
invention, there is provided an electron-emitting  
25 device comprising the device structure that a  
semiconductor layer is formed between opposing



1 electrodes , and fine particles are arranged inside  
the layer, or on the layer, of said semiconductor  
layer in a dispersed state.

5 BRIEF DESCRIPTION OF THE DRAWINGS

~~Fig. 1 to Fig. 7 are cross sections  
illustrating vertical type electron emitting devices  
of the present invention.~~

Fig. 8 is a perspective view illustrating an  
10 electron-emitting device of the present invention  
having an insulating layer comprising fine particles  
arranged in a dispersed state;

Fig. 9 and Fig. 10 are cross sections along  
the line A to B in Fig. 8;

15 ~~Fig. 11 and Fig. 14 are views explanatory of  
the preparation processes of electron emitting devices  
of the present invention.~~

~~Fig. 12, Fig. 13, Fig. 15 and Fig. 16  
diagrammatically illustrate electron-emitting devices  
20 according to other embodiments of specific structures  
of the present invention.~~

~~Fig. 17 to Fig. 27 diagrammatically illustrate  
electron-emitting devices of the present invention  
having a semiconductor layer comprising fine particles  
25 arranged in a dispersed state.~~

~~Fig. 28 to Fig. 36 diagrammatically illustrate~~

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1 ~~electron-emitting devices according to other~~  
~~embodiments of specific structures of the present~~  
~~invention.~~

Figs. 37(a) and 37(b) illustrate  
Fig. 37 diagrammatically illustrates an

5 electron-emitting device comprising two kinds of fine  
particles arranged in a dispersed state; and

Fig. 38 is a view illustrating a conventional  
electron-emitting device

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10 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

More specifically, the present invention is an  
electron-emitting device comprising a laminate  
comprising an insulating layer disposed between a pair  
of opposing electrodes, wherein an electron-emitting  
15 region insulated from the electrodes is provided at a  
side end surface of the insulating layer formed at the  
part at which the electrodes oppose each other, and  
electrons are emitted from the electron-emitting  
region by applying voltage between the electrodes.

20 Fig. 1 diagrammatically illustrates a first  
embodiment of the electron-emitting device of the  
present invention. In the figure, the numerals 1 and  
2 denote electrodes for obtaining electrical  
connection; 3, an electron-emitting region; 4, a  
25 substrate; and 5, an insulating layer.

In Fig. 1, the electron-emitting device of the

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1 present invention comprises a laminate comprising the  
insulating layer 5 disposed between a pair of the  
electrodes 1 and 2 opposing each other at their end  
portions, wherein the electron-emitting region 3  
5 insulated from the electrodes is provided at a side  
end surface of the insulating layer 5 formed at the  
opposing part at which the electrodes 1 and 2 oppose  
each other, and electrons are emitted from the  
electron-emitting region 3 by applying voltage between  
10 the electrodes 1 and 2.

In the above electron-emitting device, the one  
corresponding to the narrow crack in the prior art can  
depend on the film thickness of the insulating layer  
5. More specifically, as illustrated in Fig. 1,  
15 taking the structure that a pair of the electrodes are  
formed above and beneath the insulating layer with  
respect to the direction of the lamination in which  
the insulating layer having the electron-emitting  
region is laminated to the substrate (hereinafter  
20 referred to as "vertical type structure") can make  
small the thickness of the insulating layer on which  
the spacing between electrodes depend.

The electron-emitting device having the  
vertical type structure has a quality more than equal  
25 to that of conventional ones without taking the  
forming means, and can give a more improved electron-

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1 emitting device that can make uniform the shape and  
width of the electron-emitting region.

In Fig. 1, the insulating layer 5 may have a  
thickness of from several angstroms to several  
5 microns, for example, from 10 angstroms to 10 microns,  
preferably from 10 to 1  $\mu\text{m}$ .

The insulating layer 5 is comprised of  $\text{SiO}_2$ ,  
 $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Al}_2\text{O}_3$  or the like, a laminated  
material of any of these, or a mixture of any of  
10 these, which is formed by vacuum deposition or  
coating. Alternatively, when the electrode 1 is  
comprised of a metal such as Al and Ta, the insulating  
layer 5 may comprise an anodic oxidation film anodized  
by electrolysis.

15 The substrate 4 is formed with glass, ceramics  
or the like, and the electrodes 1 and 2 are formed  
with Au, Ag, Cu, Mo, Cr, Ni, Al, Ta, Pd, W or the  
like, or an alloy of any of these, or carbon, etc.

The electrodes 1 and 2 may have a thickness of  
20 from several hundred angstroms to several  $\mu\text{m}$ ,  
preferably from 0.01 to 2  $\mu\text{m}$  in the case of the  
vertical type. Formation methods include vacuum  
deposition, photolithography, and printing.

An outline of the method of preparing the  
25 electron-emitting device according to the present  
invention can be specifically described based on Fig.

1 1 as follows:

The electrode 1 is vapor deposited on the substrate 4, and then subjected to patterning to give a desired shape as exemplified by a stripe.

5 Thereafter, the insulating layer 5 is formed by means of vacuum deposition, coating or the like. Thickness of the insulating layer depends on the dielectric strength depending on materials for the insulating layer, and the threshold voltage at which emission of  
10 electrons begins by the voltage applied between the electrodes 1 and 2. Usually, to set the threshold voltage to from 10 to 20 V, this film thickness must be 1 micron or less. After formation of the insulating layer 5, the electrode 2 is formed by  
15 conventional vacuum deposition, printing, coating or the like process, and then the electrode 2 and the insulating layer 5 are so subjected to patterning along the pattern of the electrode 1 that they may partly overlap with the electrode 1 in the same  
20 pattern. (See Fig. 1.) In that occasion, the electron-emitting region 3 may be obtained by disposing an electron-emitting layer 3a between the insulating layers 5a and 5b according to the manner as described later, or may be obtained by disposing electron-  
25 emitting bodies 3b at the side face of the insulating layer 5.

1        Good results can also be exhibited not only by  
taking the structure in which the electrodes 1 and 2  
overlap as shown in Fig. 1, but also by an electron-  
emitting device comprising the electron-emitting  
5 region 3 disposed at a side end surface defined  
between a pair of electrodes 1 and 2 that oppose at  
their end portions but have no overlap as shown in  
Fig. 2

      The electron-emitting region 3 is formed by  
10 disposing an electron-emitting layer 3a in the  
insulating layer 5 comprised of a material readily  
capable of field emission of electrons, a material  
readily capable of secondary electron emission, or a  
material readily capable of emitting electrons by  
15 electron bombardment and having strong thermal  
resistance and corrosion resistance, as exemplified by  
metals such as W, Ti, Au, Ag, Cu, Cr, Al and Pt,  
oxides such as  $\text{SnO}_2$ ,  $\text{In}_2\text{O}_3$ , BaO and MgO, or carbon or  
a mixture of any of the above, each having a low work  
20 function and high thermal resistance, utilizing vacuum  
deposition, coating, sputtering deposition, dipping,  
or the like process.

      Alternatively, it may comprise a thin coating  
comprising superfine particle powder of metals as  
25 exemplified by Au, Ag, Cu, Cr and Al, or can be also  
formed by arranging electron-emitting bodies 3b at the

1 side face of the insulating layer 5 comprising a thin  
coating of the material as described for the above  
electron-emitting layer 3a. (Utilizable coating  
methods include spreading, all sorts of vacuum  
5 deposition, and dipping.)

Electrode spacing 6 in Fig. 1 and Fig. 2  
somewhat differs, but in approximation may desirably  
be formed in from several ten angstroms to several  $\mu\text{m}$ .  
preferably from several ten angstroms to 2  $\mu\text{m}$ , and  
10 more preferably from 10 angstroms to 1  $\mu\text{m}$ .

An outline of a method for preparing the  
electron-emitting device illustrated in Fig. 2 will be  
described below.

An insulating layer 5 is formed on a substrate  
15 4, and a stepped portion is formed by patterning.

Thereafter the electrodes 1 and 2 are simultaneously  
formed into films so that the stepped portion may not  
be covered by the electrodes, thus forming the  
electrode spacing 6. Accordingly, the electrode  
20 spacing 6 depends on thickness of the electrode formed  
at the stepped portion set with the film thickness of  
the insulating layer 5. The film formation of this  
electrode is carried out usually by using vacuum film  
formation or a similar process, so that it is possible  
25 to control the film thickness in high precision.

Thus, for the electrode spacing 6, small spacing of

1 several ten angstroms can be readily obtained in high  
precision.

The stepped portion at which the electrode  
spacing 6 is formed can also be obtained by pattern  
5 etching of the substrate 4 itself, without using the  
insulating layer 5. There is also available a method  
in which the electrodes 1 and 2 are formed on this  
stepped portion to obtain an electron-emitting device.  
(See Fig. 7.)

10 Taking the structure that a pair of the  
~~electrodes~~<sup>electrodes</sup> opposing each other have no mutual overlap  
as illustrated in Fig. 2 can bring about a more  
superior electron-emitting device suffering less  
increase in driving power consumption that may be  
15 otherwise caused by increase in the electrical  
capacity at the part at which the electrodes overlap,  
less delay of driving electric signals, and less  
influence by dielectric strength or pinholes of the  
insulating layer.

20 On the other hand, the electron-emitting  
device having the structure as shown in Fig. 7 makes  
it unnecessary for the electrodes to be held by the  
insulating layer, and makes it possible also to obtain  
the spacing of the opposing electrodes by utilizing  
25 the stepped portion, so that if, for example, the  
electrodes-supporting substrate itself is etched to

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1 provide the stepped portion, there is given an  
electron-emitting device that can be obtained without  
formation of any insulating layer, making simple its  
preparation processes.

5 The electron-emitting device of the present  
invention may further have the structure as shown in  
Fig. 4.

In Fig. 4, the numerals 1 to 5 denotes the  
same as those in Fig. 3. In the present figure, the  
10 numeral 8 denotes an intermediate layer, which is  
disposed between the insulating layer 5 and the  
electrode 2 to constitute a multi-layer electrode.  
The intermediate layer 8 plays a role to bring about  
the effect of preventing sputtering damage caused by  
15 electrons or ions in the electrode 2, or the effect of  
bringing electrons to more readily emit. As the  
intermediate layer 8, high-melting materials as  
exemplified by W,  $\text{LaB}_6$ , carbon, TiC and TaC may be  
used to make small the sputtering damage, and  
20 materials having a low work function as exemplified by  
 $\text{SnO}_2$ ,  $\text{In}_2\text{O}_3$ ,  $\text{LaB}_6$ , BaO, CS and CSO may be used to  
achieve improvement in electron emission efficiency.

There may be also used a laminate, or a  
✓ mixture, comprising these both materials. Of course,  
25 similar effect can be obtained also when the  
intermediate layer 8 is provided on the electrode 1 to

1 give a multi-layer electrode. Further, when both the  
electrodes are made to comprise the multi-layer  
electrode, suitable materials for the intermediate  
layer 8 can be selected for each electrode. Also, a  
5 laminate comprising an insulating layer 5a, an  
electron-emitting layer 3a and an insulating layer 5b  
may be made to comprise a multi-layer laminate  
constituted of, for example, an insulating layer 5a,  
an electron-emitting layer 3a, an insulating layer 5b,  
10 an electron-emitting layer 3a, an insulating layer 5a,  
and an electron-emitting layer 3a. At least one layer  
of the multi-layer electrodes, as exemplified by the  
electrode 2 in Fig. 4, may further preferably be  
comprised of a material having a high electrical  
15 conductivity. This is because the materials for the  
intermediate layer 8 are materials having relatively  
low electrical conductivity as for electrode wiring  
materials.

An excessively high wiring resistance of a  
20 device may cause an increase in the power consumption  
or a delay in the driving signals, resulting in  
undesirableness in driving the device. For this  
reason, the materials having high electrical  
conductivity is used in the electrode 2 to keep to a  
25 low level the wiring resistance of the whole multi-  
layer electrode. Usable as the materials having high

1 electrical conductivity are Ag, Al, Cu, Cr, Ni, Mo,  
Ta, W, etc.

In Fig. 4, when the electron-emitting layer 3a  
comprises the material suffering less sputtering  
5 damage or having a low work function, the intermediate  
layer 8, or the electrode 1 and the intermediate layer  
8, may be formed with use of the same materials as in  
the electron-emitting layer 3a.

The present invention further provides an  
10 electron-emitting device having a device structure  
wherein an insulating layer is formed between  
electrodes opposing each other, and fine particles are  
contained in said insulating layer and at the same  
time arranged in a dispersed state.

15 Taking the above described device structure of  
the present invention not only can solve the problems  
in the prior art previously discussed, but also can  
provide an electron-emitting device capable of  
obtaining an emitted electric current of high density  
20 by using a low electric power and also capable of  
controlling the island spacing, island size of the  
islands previously mentioned. This electron-emitting  
device will be described below with reference to the  
drawings.

25 In Fig. 8, provided on a substrate 4 such as  
glass and ceramics is an insulating layer 11, and

1 further thereon electrodes 1 and 2 comprised of low-  
resistance materials for use in voltage application  
are provided giving minute spacing to form a  
discontinuous electron-emitting region 10 comprising  
5 fine particles 9 dispersed between them. Though not  
shown in the drawing, a space is taken at an upper  
area of the electron-emitting region to provide there  
a lead-out electrode for leading out emitted  
electrons. Application of voltage between the  
10 electrodes 1 and 2 in vacuo (this voltage is assumed  
as  $V_f$ ) brings about flow of electricity between the  
electrodes ( $I_f$ ) to apply voltage using the lead-out  
electrode as the anode, so that electrons are emitted  
from the electron-emitting region in the direction  
15 substantially vertical to the paper surface in the  
drawing. (The electric current for this electron  
emission is assumed as  $I_e$ .)

Fig. 9 and Fig. 10 diagrammatically illustrate  
cross sections in the A-B direction in Fig. 8. In the  
20 present figures, the fine particles on the substrate 4  
may preferably have a particle diameter of from  
several ten angstroms to several  $\mu\text{m}$ , and the spacing  
between respective fine particles may further  
preferably be formed in the range of from several ten  
25 angstroms to several  $\mu\text{m}$ .

Materials for the fine particles used in the

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1 present invention may cover a very wide range, and  
almost all of conductive materials including usual  
metals, semimetals and semiconductors. Particularly  
suitable are usual cathode materials having properties  
5 such as low work function, a high melting point and  
low vapor pressure, thin film materials capable of  
forming the surface conduction electron-emitting  
device by the conventional forming treatment, and  
materials having a large coefficient of secondary  
10 electron emission.

Appropriate materials may be selected from  
such materials according to purposes and used as the  
fine particles, so that a desired electron-emitting  
device can be formed.

15 Specifically, they may include, for example,  
borides such as  $\text{LaB}_6$ ,  $\text{CeB}_6$ ,  $\text{YB}_4$ , and  $\text{GdB}_4$ , carbides  
such as  $\text{TiC}$ ,  $\text{ZrC}$ ,  $\text{HfC}$ ,  $\text{TaC}$ ,  $\text{SiC}$  and  $\text{WC}$ , nitrides such  
as  $\text{TiN}$ ,  $\text{ZrN}$  and  $\text{HfN}$ , metals such as Nb, Mo, Rh, Hf,  
Ta, W, Re, Ir, Pt, Ti, Au, Ag, Cu, Cr, Al, Co, Ni, Fe,  
20 Pb, Pd, Cs and Ba, metal oxides such as  $\text{In}_2\text{O}_3$ ,  $\text{SnO}_2$   
and  $\text{Sb}_2\text{O}_3$ , semiconductors such as Si and Ge, carbon,  
and AgMg. The present invention is by no means  
limited by the above materials. Moreover, in the  
present invention, it may also be practiced to select  
25 different materials among the above materials and  
disperse fine particles of two or more kinds of

1 different materials.

A method for preparing the device illustrated in Fig. 8 will be described below.

Fig. 11 <sup>A</sup>(1) to <sup>E</sup>(5) illustrate cross sections  
5 of a device for each preparation step.

(1) The surface of a substrate 4 comprised of glass or ceramics is degreased and cleaned.

(2) An insulating layer 11 comprised of low-  
melting point glass is formed into a film on the  
10 surface of the substrate 4 according to liquid-coating  
baking, printing baking, vacuum deposition, or the  
like process. Desirable as materials for the low  
melting point glass are those having a softening point  
temperature lower than the distortion point  
15 temperature of the substrate and at the same time  
having a coefficient of thermal expansion close to  
that of the substrate. In general, a lead oxide type  
low melting glass has a softening point of about 400°C  
and also has a coefficient of thermal expansion close  
20 to the coefficient of thermal expansion of a soda lime  
glass substrate generally used. The insulating layer  
11 may desirably be formed to have a thickness in the  
range of from several ten angstroms to several ten  $\mu\text{m}$   
in approximation.

25 (3) On the insulating layer obtained in (2),  
electrodes 1 and 2 are formed according to vacuum

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1 deposition, photolithoetching, lifting-off, printing,  
or the like process.

Usable as electrode materials are the same  
materials as those described in relation to Fig. 1,  
5 i.e. Au, Ag, Cu, Mo, Cr, Ni, Al, Ta, Pd and W, or an  
alloy of any of these or carbon, etc., and the  
electrodes 1 and 2 may also suitably have a thickness  
of from several hundred angstroms to several  $\mu\text{m}$ ,  
preferably from 0.01 to 2  $\mu\text{m}$ .

10 As to the dimension of electrode spacing L,  
the electrodes may suitably oppose each other with a  
space of from several hundred angstroms to several ten  
 $\mu\text{m}$ , and spacing width W may suitably be approximately  
from several  $\mu\text{m}$  to several mm. However, they are by  
15 no means limited to these dimensions.

(4) Next, the fine particles 9 are coated on the  
electrode gap region obtained in (3). A dispersion of  
fine particles are used in the coating. Fine  
particles and an additive to promote dispersion of the  
20 fine particles are added in an organic solvent  
comprised of butyl acetate, alcohol or the like,  
followed by stirring or the like to prepare the  
dispersion of fine particles. This fine particle  
dispersion is coated on the surface of a specimen  
25 according to dipping, spin coating or the like  
process, and then calcination is carried out for about

1 10 minutes at a temperature at which the solvent or  
the like may be evaporated, for example, at 250°C.  
Thus the fine particles are arranged on the surface of  
the insulating layer 11 in the electrode spacing L.  
5 Of course, the fine particles 9 are arranged on the  
whole surface of the specimen, but no difficulty is  
brought about as there is applied substantially no  
voltage to the fine particles 9 outside the electrode  
spacing L when electrons are emitted. This is  
10 accordingly not shown in the drawing. Arrangement  
density of the fine particles 9 may vary depending on  
the coating conditions and how to prepare the fine  
particle dispersion, and the amount of electric  
currents flowing to the electrode spacing L may also  
15 vary in accordance with this. In addition to the  
above formation by coating, also available as a method  
for dispersing the fine particles 9 to the electrode  
gap region obtained in (3) is, for example, a method  
in which a solution of an organic compound is coated  
20 on the substrate followed by thermal decomposition to  
form metal particles. In regard to materials feasible  
for vacuum deposition, the fine particles can be also  
formed by control of vacuum deposition conditions such  
as substrate temperature or by a means like vacuum  
25 deposition such as masked vacuum deposition.

(5) After this, the specimen obtained through the

241



1 steps up to (4) is heated to a temperature higher than  
the softening point of the low-melting glass  
constituting the insulating layer 11, for example, to  
450°C if it is the lead oxide type low-melting glass,  
5 to carry out baking for about 20 minutes. By this  
procedure, the fine particles 9 arranged on the  
insulating layer 11 comprised of the low <sup>Melting</sup> ~~meting~~ glass  
penetrate into the low-melting glass, resulting in  
being included (or enclosed) into the insulating layer  
10 11, or included to the extent that at least part of a  
particle is exposed from the insulating layer 11, and  
then fixed there.

Whether the fine particles 9 are brought into  
the state that all of them are included into the  
15 insulating layer 11 or the state that only part of a  
particle penetrates into the insulating layer 11 in  
the state that the surface remains exposed, may be  
adjusted by selecting the baking temperature in the  
step (5).

20 The higher the baking temperature is, the more  
readily the fine particles 9 are penetrated deeply  
into the insulating layer 11, and are included and  
fixed. A lower baking temperature may make it  
difficult for the fine particles 9 to penetrate into  
25 the insulating layer 11, and tend to make them fixed  
in the exposed form.

1        Some of the materials such as Pd listed in the  
above embodiment may be covered on their surfaces with  
oxide films as a result of heating in the above step  
(5), resulting in decrease in the amount of the  
5 electric current flowing to the electrode spacing L.  
Therefore, a step of pickling to remove the oxide film  
may be introduced if necessary.

In the present invention, the device may also  
be formed by bringing the fine particles 9 to be  
10 completely included into the insulating layer 11 and  
thereafter carrying out etching to bring part of each  
particle to be exposed.

Not only the device prepared according to the  
above preparation steps, having the structure as  
15 (A) - 11(E) illustrated in Fig. 11, but also the devices having  
the structure illustrated in Fig. 12 and Fig. 13(a)  
and (b) can also exhibit good results.

Preparation processes in Fig. 12 will be  
described.

20        Electrodes 1 and 2 are formed on a substrate  
4, on which a fine particle dispersion or a dispersion  
prepared by mixing low-melting frit glass into an  
organic metal compound solution is coated in the  
vicinity of the electrode spacing region L, followed  
25 by baking at a temperature higher than the softening  
point of the low-melting frit glass crystalline

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1 melting point to bring the fine particles to be  
included into an insulating layer 11 comprised of the  
low-melting glass, or bring at least part thereof to  
be exposed, and then fixed. Here, the baking  
5 temperature set to a higher degree (as exemplified by  
650°C enables the smoothing of the insulating layer 11  
to make a continuous film.

In the figure, the insulating layer 11 may  
preferably be formed to have a film thickness of from  
10 several ten angstroms to several  $\mu\text{m}$  in approximation.

Here, a liquid coating insulating layer (as  
exemplified by Tokyo Ohka OCD, a  $\text{SiO}_2$  insulating  
layer) may be used in place of the low-melting frit  
glass.

15 In the instance where the liquid coating  
insulating layer is used, it is also possible to  
obtain the electron-emitting device of the present  
invention in the following manner: First, the  
insulating layer 11 containing the fine particles 9 is  
20 built up on the substrate 4 according to liquid  
coating. Namely, it can be obtained by coating the  
fine particles mixed and dispersed in a liquid coating  
preparation, on a substrate by spin coating, dip  
coating or the like.

25 Next, electrodes are formed on the insulating  
layer 11 according to the above processes such as

1 vacuum deposition to make up an electron emission  
device.

Taking said process, the fine particles are  
coated on the substrate in the state that they are  
5 mixed and dispersed in the liquid coating preparation  
or the like for obtaining the insulating layer, and  
therefore, even after the coating and baking, they  
remain dispersed in a good state in the film formed by  
coating the liquid coating preparation for obtaining  
10 the insulating layer. Accordingly, the fine particles  
suffer less agglomeration, and can be uniformly  
dispersed in the insulating layer obtained by the  
liquid coating preparation.

Also, since in the present structure the  
15 insulating layer containing fine particles is first  
formed on the substrate, the substrate surface before  
formation of the insulating layer is usually a uniform  
surface without any particular pattern or roughness.  
Accordingly, since the insulating layer containing the  
20 fine particles in its uniform surface is formed by  
coating and baking, there is no non-uniformity in the  
film thickness or fine particle dispersion owing to  
coating unevenness at the part of the pattern or  
roughness, so that a support layer in which the fine  
25 particles are dispersed can be uniformly formed on the  
substrate surface. Obtaining the insulating layer

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1 that is uniform like this can make small the  
irregularity or the like in device characteristics  
when a number of electron-emitting devices are  
provided on the same substrate.

5           Moreover, although in the present structure an  
in-air heating step at about  $400^{\circ}\text{C}$  or more becomes  
necessary, for example, when the oxide type insulating  
layer is formed using the liquid coating preparation,  
the electrodes themselves do not pass through the  
10 heating step because the insulating layer formation  
heating is carried out before formation of the  
electrodes. Therefore, no account is required to be  
taken for the thermal oxidation of electrodes or  
thermal diffusion with respect to the insulating  
15 layer, thus enabling expansion of the range of  
selection for electrode materials.

Accordingly, the materials may be  
appropriately selected depending on the conditions  
such as dielectric strength, thermal resistance,  
20 workability, oxidation resistance, life, specific  
resistance, and amount of electric current that can be  
taken out. The materials for the insulating layer may  
include, as previously described,  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ,  
 $\text{Ta}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$ , or a laminate or mixture of any of  
25 these. The film thickness may be from about 10  
angstroms to several um or so, which is the thickness

1 necessary for the fine particles 9 to be dispersed and  
fixed.

The electron-emitting device may also have the  
structure as illustrated in Fig. 13<sup>(a) and 13(b)</sup>

5 In the electron-emitting device illustrated in  
Fig. 13, a fine particle dispersion prepared by mixing  
the low-melting frit glass for the insulating layer 11  
is coated (here, carried out in the same manner as  
described in relation to Fig. 12), and thereafter the  
10 insulating layer 11 is formed into a discontinuous  
island-shaped film by setting the baking temperature  
to somewhat lower degree (for example, about 500°C).

In the electron-emitting device illustrated in  
Fig. 13, the insulating layer 11 does not entirely  
15 cover the electrode spacing L as so illustrated in the  
figure, so that it takes the form that the electrode  
ends of the electrodes 1 and 2, on the side of the  
electrode spacing L, i.e., the part at which a highest  
electric field is generated, is connected with the  
20 surface and inside of the insulating layer 11. For  
this reason, the degree of freedom of the electric  
current flow path becomes greater, so that the amount  
of electric current flowing between the electrodes can  
be more increased than the device of Fig. 12.

25 Both the electron-emitting device of Fig. 12  
and the electron-emitting device of Fig. 13<sup>(A) and 13(B)</sup> in which

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1 the insulating layer and the fine particles can be  
formed simultaneously, have the advantage that the  
preparation steps can be simplified.

The electron-emitting device of the present  
5 invention may further comprise a device having the  
structure as illustrated in Fig. 14(E).

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In Fig. 14(A) to 14(E), the numeral 4 denotes a substrate;  
1 and 2, electrodes; 9, fine particles; and 11, an  
insulating layer.

10 Fig. 14(A) to (E) illustrate cross sections  
of a device for each preparation step.

1) The surface of the substrate 4 is degreased  
and cleaned.

✓ 15 2) The electrodes 1 and 2 are formed in the same  
manner as in (3) in Fig. 11.

✓ 3) The fine particles are dispersed in the same  
manner as in step (4) in Fig. 11.

4) The insulating layer 11 is formed by a method  
of EB vacuum deposition, sputtering, or vacuum  
20 deposition such as plasma CVD, heat CVD or the like  
process. Usable as materials for the insulating layer  
11 are oxides such as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , nitrides such as  
 $\text{Si}_3\text{N}_4$ , carbides such as  $\text{SiC}$  and  $\text{TiC}$ , as well as glass  
obtained by vacuum deposition or solution-coated  
25 baking, and insulating layers comprising organic  
polymers such as polyimides. Also, the layer 11 may

1 desirably have a film thickness of from several 10  
angstroms to several  $\mu\text{m}$ . Here, in general, the  
insulating layer 11 is deposited also on the surface  
of fine particles 9, and so deposited that the  
5 particle diameters of the fine particles 9 may produce  
convexes.

The electron emission device prepared  
according to the above steps 1) to 4) can serve as a  
device having far superior characteristics as compared  
10 with the conventional devised prepared using the  
forming. In the electron-emitting device of the  
present invention, even the device obtained according  
to the steps 1) to 4) can exhibit sufficiently good  
characteristics, but more preferred is a device  
15 applied with the following step 5), since the extent  
of exposure of the fine particles fixed in the  
insulating layer can be made adjustable by adjusting  
the deposit thickness of the insulating layer and the  
amount of etching, and furthermore it becomes possible  
20 to control the electric current between electrodes and  
also control the amount of electron emission.

5) Etching is applied on the surfaces of the  
convexes of the insulating layer 11 obtained in 4).  
For example, ion milling may be carried out in the  
25 state that the specimen is obliquely set, so that the  
surfaces of the convexes of the insulating layer 11



1 are etched. As a result, there is given the structure that part of each fine particle 9 is exposed from the insulating layer 11 at the etched portions and also fixed in the insulating layer 11.

5 In addition, in the above steps 1) to 5), the low-melting glass may be used as the material for the insulating layer 11 and, after step 5) in Fig. 14<sup>(A-E)</sup>, the specimen may be baked at a temperature higher than the softening point of the low-melting glass, so that the  
10 fine particles 9 can be further firmly fixed in the insulating layer 11 comprised of the low-melting glass. This makes it possible to provide a further stable electron-emitting device.

The electron-emitting device of the present  
15 invention may also comprise those as illustrated in Fig. 15 (a) and (b) and Fig. 16 (a) and (b).

In Fig. 15, the numeral 12 denotes a substrate comprising metals 13 such as Ag, Ba, Pb, W and Sn or metal oxides 13 such as BaO, PbO and SnO<sub>2</sub> deposited in  
20 porous glass. The numerals 1 and 2 denote electrodes provided on the substrate.

Usable as the above porous glass are <sup>Vycor</sup>~~Vicor~~ glass available from Corning Glass Works or porous glass MPG available from Asahi Glass Co., Ltd., and  
25 those having a pore size of from 40 angstroms to 5 μm, more preferably having a pore size of from 100

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1 angstroms to 0.5  $\mu\text{m}$ . Fine particles of metals or  
metal oxides of the size equal to or smaller than the  
pore size are deposited in the pores. The present  
embodiment may not be limited to the porous glass, and  
5 may be worked using those obtained by roughening the  
glass surface with an aqueous hydrofluoric acid  
solution or other porous insulating substrates.

Bringing metals to be deposited and fixed in  
the pores of porous glass can be achieved by commonly  
10 available methods as exemplified by a method in which  
porous glass is impregnated with an aqueous solution  
of a nitrate such as  $\text{AgNO}_3$ ,  $\text{Ba}(\text{NO}_3)_2$  and  $\text{PbNO}_3$  or an  
aqueous sulfuric acid solution, followed by drying and  
thereafter baking in a reducing atmosphere. To  
15 deposit the metal oxides, the deposited metals may be  
baked at a suitable temperature and in an atmosphere  
of oxygen.

In bringing the metals or metal oxides to be  
projected from the surface of porous glass, the glass  
20 surface may be treated for 1 minute with a  
hydrofluoric acid solution, followed by washing and  
drying. A desired substrate 12 can be thus prepared.

The above substrate 12 may more preferably  
have a thickness of 0.5  $\mu\text{m}$  or more because of the  
25 roughness on the surface of porous glass.

✓ In Fig. 16, the numeral 14 denotes a glass

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1 substrate commonly called as colored glass, which is  
glass that contains metal colloid fine particles 15.  
The numeral 1 or 2 denotes an electrode provided on  
the substrate. The metal colloid fine particles in  
5 the colored glass may suitably have a particle  
diameter of from 20 angstroms to 6,000 angstroms, more  
desirably from 100 angstroms to 2,000 angstroms.  
Also, the density of the fine particles, though  
variable depending on the particle diameter or  
10 materials for the fine particles, may suitably be in  
such a state that particles are spatially apart and  
electrically connected in the vicinity of a drive  
voltage. To make such colored glass, it can be  
15 readily prepared by a commonly often used technique,  
namely, a method in which colorant raw materials such  
as  $\text{AuCl}_3$  and  $\text{AgNO}_3$  are dissolved in main components of  
the glass, which is then subjected to heat treatment  
for 10 to 20 minutes at temperatures of from  $600^\circ\text{C}$  to  
900 $^\circ\text{C}$  to deposit gold colloid or silver colloid fine  
20 particles in the glass. In the substrate prepared  
according to such a commonly available method, the  
metal fine particles are little deposited out of the  
glass surface, and therefore have good smoothness of  
the substrate surface on which the electrodes are  
25 formed, thus bringing about the advantage that the  
electrodes in this device can be made to have a

1 smaller thickness.

In this device, after the metal fine particles were deposited in the glass, the substrate surface may also be treated with an aqueous hydrofluoric acid  
5 solution in the same manner as in the device described in relation to the above Fig. 15 so that the metal colloids may be protruded in a large number from the glass substrate surface, thus obtaining the effect as aimed in the present invention.

10 The present invention further provides an electron-emitting device characterized by a device structure, comprising a semiconductor layer formed between opposing electrodes, and fine particles further arranged in a dispersed state on said  
15 semiconductor layer.

In the electron-emitting device of the present invention, application of a voltage between the electrodes brings about emission of electrons from the fine particles which are conductive.

20 Taking such a device structure not only can solve the problems involved in the prior art previously discussed, but also can provide an electron-emitting device capable of obtaining emitted electric currents with a low electric power and in a high  
25 density.

Description will be made below on the basis of

36

1 Fig. 17.

In the figure, electrodes 1 and 2 are provided on a substrate 4, giving minute spacing to form a discontinuous electron-emitting region comprising fine particles 9 dispersed between them. The numeral 16 denotes a semiconductor layer formed at least at an electrode spacing region L.

Fig. 18 is a diagrammatical cross section in the C-D direction in Fig. 17. In the figure, the kind, particle diameter and spacing between fine particles on the substrate 4 are as described in relation to Fig. 8.

A method for preparing of the device illustrated in Fig. 17 will be described below.

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12/5/97 15 Fig. 19 <sup>A</sup>(A) to <sup>C</sup>(C) illustrate cross sections of a device for each preparation step.

(1) The surface of a substrate 4 comprised of glass or ceramics is degreased and cleaned.

(2) On the insulating layer obtained in (1), electrodes 1 and 2 are formed according to vacuum deposition, photolithoetching, lifting-off, printing, or the like process.

(3) Next, the fine particles 9 are coated on the electrode gap region obtained in (2). A dispersion of fine particles are used in the coating. Fine particles and an organic binder to promote dispersion

1 of the fine particles are added in an organic solvent  
comprised of butyl acetate, alcohol, ketone or the  
like, followed by stirring or the like to prepare the  
dispersion of fine particles. Usable as the organic  
5 binder are butyral resins, acrylic resins, vinyl  
chloride-vinyl acetate copolymers, phenol resins,  
nylons, polyesters and urethanes.

Here, an example of methods for preparing the  
dispersion of the fine particles is set out below.

10 Fine particles,  $\text{SnO}_2$  1 g  
(fine particle diameter: 100 to 1,000 angstroms)  
Organic solvent, MEK (methyl ethyl ketone) :  
cyclohexane = 3 : 1 1,000 cc  
Organic binder, butyral 1 g

+360X  
15 The above materials were stirred in a paint shaker for  
three hours <sup>WITH</sup> glass beads to make a dispersion.

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This fine particle dispersion is coated on the  
surface of a specimen according to dipping, spin  
coating or the like process, and then baking is  
20 carried out for about 10 minutes at a temperature at  
which the solvent or the like may be evaporated and  
also the organic binder is carbonized to give a  
semiconductor layer, for example, at  $250^\circ\text{C}$ . Thus the  
semiconductor layer 16 and the fine particles 9 are  
25 arranged in the electrode spacing L. Of course, the  
semiconductor layer 16 and the fine particles 9 are

In addition to the above formation by coating, also available as a method for dispersing the fine particles 9 to the electrode gap region obtained in 15 (2) is, for example, a method in which a solution of an organic compound is coated on the substrate followed by thermal decomposition to form metal particles. As an example, a solution is prepared using materials shown below:

Fine particle material: Pd organic metal compound (weight calculated as Pd metal)

Organic solvent: Butyl acetate 1,000 g

Organic binder: Butyral 1 g

25 This Pd organic metal compound solution is coated,  
followed by heating, so that the fine particles 9

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1 comprising Pd and the insulating layer 16 can be  
obtained.

The semiconductor layer 16 comprises a film  
mainly constituted of the carbon obtained by the  
5 baking. This is a semiconductor layer having an  
electrical specific resistance of about  $1 \times 10^{-3}$   
ohm.cm or more.

In the specimen obtained according to the  
above steps, the thickness of the semiconductor layer  
10 16 becomes smaller than the particle diameter of the  
fine particles 9. In other words, it has the  
structure that the fine particles 9, though embedded  
in the semiconductor layer 16, are fixed in the manner  
that they are partly protruded (Fig. 18).

15 In the embodiment having been described above,  
the fine particles 9 has the structure that they  
protrude from the semiconductor layer 16. Here, the  
fine particles 9 may be covered with a carbon film  
obtained by further coating only the organic binder  
20 solution on the surface of this device followed by  
baking, so that there can be given the structure that  
the fine particles 9 are included into the  
semiconductor layer 16 as illustrated in Fig. 20.

The ratio of carbon to fine particles in the  
25 coating solution may be changed to increase the  
carbon, and also the amount of coating may be



1 increased, so that there can be also given the  
structure that the fine particles 9 are included into  
the semiconductor layer 16 or at least part thereof  
has protruded from the semiconductor layer as  
5 illustrated in Fig. 21.

The devices having been described above has  
the feature that the production steps can be  
simplified since the semiconductor layer 16 is formed  
in the same step as for arrangement of the fine  
10 particles 9.

It is also possible to prepare the  
semiconductor layer 16 from materials other than the  
carbon, namely, semiconductor materials obtained by  
coating or printing and baking, as exemplified by a  
15 solution containing Si, Ge, Se or the like.  
Accordingly, a semiconductor layer having desired  
characteristics can be obtained by selecting the  
conditions for the preparation and coating of the  
solution of these materials and for the baking. Also  
20 in using these semiconductor layers, there is retained  
the feature that the fine particles can be arranged in  
the same step.

The electron-emitting device of the present  
invention may also comprise an electron-emitting  
25 device having the structure as shown in Fig. 22.

A method of preparing the electron-emitting

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1 device illustrated in Fig. 23, <sup>A</sup>2) to <sup>D</sup>4) will be described. Cross sections of a device are illustrated in succession to describe below an example of the preparation method.

5 1) The surface of a substrate 4 is degreased and cleaned.

2) On the substrate obtained in 1), formed is a semiconductor layer 16 obtained by vacuum deposition, coating or printing and baking.

10 Usable as the above semiconductor layer are an amorphous silicon semiconductor film or crystallized silicon semiconductor film obtained by vacuum deposition, a compound semiconductor film, and a semiconductor film obtained by coating or printing and  
15 baking.

For example, there can be formed a hydrogenated amorphous silicon (A-Si:H) semiconductor layer obtained by plasma CVD. This semiconductor layer has a film thickness of approximately from 50  
20 angstroms to 10  $\mu\text{m}$ .

3) Electrodes 1 and 2 are provided in the same manner as in (2) in Fig. 19.

4) Fine particles 9 are provided in the same manner as in (3) in Fig. 19. It is preferred to  
25 decrease the amount of carbon in the coating solution or reduce it to zero to make small the thickness of

1 the carbon film semiconductor layer formed at the  
electrode spacing region L. This is because the  
effect of the semiconductor layer 16 can be better  
brought out by allowing an electric current  $I_f$  flowing  
5 to the electrode spacing L to flow to the  
semiconductor layer 16 and the fine particles 9 as  
much as possible.

In the device having such structure, it is  
also possible to use fine particles feasible for  
10 vacuum deposition. With a material applicable to  
vacuum deposition, the fine particles can be formed by  
control of vacuum deposition conditions such as  
substrate temperature or by a means like vacuum  
deposition such as masked vacuum deposition.

15 In the electron-emitting device obtained  
according to the above 1) to 4), the semiconductor  
layer and the fine particles are each formed in a  
separate step, resulting in a greater degree of  
freedom in the conditions for forming the  
20 semiconductor layer. Accordingly, it becomes more  
possible to adjust characteristics of the  
semiconductor layer 16. For example, changing the  
amount of an impurity dope and selecting suitable  
conditions for formation in forming a semiconductor  
25 makes it able to readily adjust the electrical  
resistance of the semiconductor layer 16.

1 Accordingly, it becomes feasible to adjust the amount  
of the electric current  $I_f$  flowing to the device, thus  
bringing about the feature that it becomes feasible to  
adjust the drive voltage of the device.

5 In the electron-emitting device of the present  
invention, the substrate itself may also comprise a  
semiconductor substrate that replaces the  
semiconductor layer 16. Fig. 24 illustrates a cross  
section of the device of this embodiment. As the  
10 semiconductor substrate 17, there can be used  
substrate materials having desired characteristics, as  
exemplified by Si wafers. Usable as methods for  
obtaining the semiconductor substrate having the  
desired characteristics are ion implantation to a  
15 semiconductor substrate or insulator substrate and the  
like methods.

This method enables adjustment of the specific  
resistance only at desired areas on the same plane.  
For this reason, in instances where electron-emitting  
20 devices are integrated in a high density, the leakage  
current among adjacent devices can be made small and  
the crosstalk can be decreased. Because of the  
arrangement on the same plane, this method further has  
the feature that no trouble such as disconnection may  
25 occur owing to poorness in step coverage on the  
stepped ends of the electrodes.

1        Fig. 25 is a cross section explanatory of  
still another electron-emitting device of the present  
invention. The respective materials are constituted  
in the manner as described above, but in the  
5 preparation steps the semiconductor layer 16 is formed  
after the electrodes 1 and 2 and the fine particles 9  
were formed. Thus the fine particles 9 are made to be  
included into the semiconductor layer 16 and fixed  
there. The surface of the semiconductor layer is  
10 thereafter shaved off by etching to give the structure  
that the fine particles 9 are fixed in the state that  
they protrude from the semiconductor layer.

Fig. 26 <sup>A</sup>(~~1~~) to <sup>E</sup>(~~5~~) successively illustrate  
cross sections of device to explain the preparation  
15 steps of the electron-emitting device illustrated in  
Fig. 5. An example of the preparation method will be  
described below.

(1)        The surface of the substrate 4 is degreased  
and washed.

20 (2)        Electrodes 1 and 2 are provided in the same  
manner as in Fig. 19(<sup>B</sup>~~2~~).

(3)        Fine particles 9 are provided in the same  
manner as in Fig. 19(<sup>C</sup>~~3~~) (preferably using a dispersion  
containing no organic binder).

25 (4)        A semiconductor 16 is formed in the vicinity  
of the electrode spacing region L. Here, in general,

12/5/97

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1 the semiconductor layer is deposited also on the  
surface of the fine particles 9, and so deposited that  
the particle diameters of the fine particles 9 may  
produce convexes.

5 (5) Etching is applied mainly on the surfaces of  
the convexes of the semiconductor layer 16 obtained in  
(4). For example, ion milling may be carried out in  
the state that the specimen is obliquely set, so that  
the surfaces of the convexes of the semiconductor  
10 layer 16 are etched. As a result, there is given the  
structure that part of each fine particle 9 is exposed  
from the semiconductor layer 16 at the etched portions  
and also fixed in the semiconductor layer 16.

If alternatively the etching step is not  
15 applied, there is given the structure that the fine  
particles 9 are included into the semiconductor layer  
16.

In all the embodiments having been described  
above, the semiconductors and fine particles are  
20 arranged in the electrode spacing region formed on a  
plane substrate, but the present invention is by no  
means limited to these forms.

For example, the electron-emitting device may  
take the form as shown in Fig. 1, i.e., the vertical  
25 type one. (See Fig. 27.) This is a device in which  
the electrodes 1 and 2 are each formed on the other

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1 side of a stepped portion of the insulating layer 5 on  
the substrate 4.

The present invention particularly further  
provides a device in which the electrodes disposed in  
5 the electron-emitting device as illustrated in Fig. 8  
are made to be disposed as in the vertical type as  
shown in Fig. 1, i.e., an electron-emitting device  
comprising a substrate provided thereon with an  
insulating layer in which fine particles are  
10 dispersed, a stepped portion formed at an end portion  
of the insulating layer on the top surface of the  
substrate, and an electrode provided each on the top  
surface of said insulating layer and on the top  
surface of said substrate; an end of each electrode  
15 being positioned at an upper end or lower end of said  
stepped portion in such a manner that at least part of  
the sidewall face at the stepped portion, of the end  
portion of said insulating layer in which the fine  
particles are dispersed may not be hidden; and  
20 electrode spacing being formed between said electrode  
ends, where electrons are emitted by applying a  
voltage between these electrodes [Fig. 28 (C)].

In Fig. 28 (a), (b) and (c), the numerals 1  
and 2 denote electrodes for obtaining electrical  
25 connection; 4, a substrate; 9, fine particles; 5, an  
insulating layer containing the fine particles in a

1 dispersed state; and 6, an electrode spacing.

In Fig. 28 (C), the electron-emitting device of the present invention is a device such that the fine particles 9 dispersed in the insulating layer 5 forming a stepped portion are arranged at the electrode spacing 6 formed between the electrodes 1 and 2 whose end portions oppose each other (but without overlap) at the stepped portion, where electrons are emitted from the fine particles 9 by applying a voltage between the electrodes 1 and 2.

An example of preparation methods will be described below in relation to Fig. 28 (a), (b) and (c).

First, the insulating layer 5 containing the fine particles 9 is built up on the substrate 4 by liquid coating or a like process [see Fig. 28 (a)].

Next, the insulating layer 5 is etched by photolithoetching so that a stepped portion is given substantially at the middle portion of the substrate 4 [see Fig. 28 (b)].

Then the electrodes 1 and 2 are deposited on the insulating layer 5 and the substrate 4 in such a manner that at least part of the sidewall of the stepped portion may not be hidden, thus forming the electrode spacing 6 [see Fig. 28 (c)].

The electron-emitting device of the present



1 invention can be obtained according to the above  
process. The present device may be placed in a vacuum  
container, a voltage may be applied to the electrodes  
1 and 2, and a lead-out electrode plate (not shown)  
5 may be disposed so as to oppose at the top surface of  
the device, to which a high voltage is applied,  
whereupon electrons are emitted from the vicinity of  
the electrode spacing 6.

In this figure, the materials for and  
10 thickness of the electrodes, materials for the fine  
particles concerned with the electron emission and  
materials for and thickness of the insulating layer  
are as described in relation to Fig. 1.

✓ It can be confirm that an electron-emitting  
15 device comprising electrodes 1 and 2 formed partly  
overlapping as illustrated in Fig. 29 (c), though  
having a slight difference in the electrode spacing,  
can also give good results.

In the device illustrated in Fig. 29 (c), an  
20 electrode 1 is first deposited and formed on a  
substrate 4 [see Fig. 29 (a)]. Thereafter an  
insulating layer 5 containing fine particles 9 and an  
electrode material 2c are deposited [see Fig. 29 (b)],  
and an electrode 2 and electrode spacing 6 are formed  
25 by photolithoetching, thus forming an electron-  
emitting device [see Fig. 29 (c)].

1           The present invention also provides an  
electron emission device as illustrated in Fig. 30,  
which is another embodiment of the electron-emitting  
device described in relation to Fig. 28 and at the  
5 same time a preferred embodiment of the electron-  
emitting device illustrated in Fig. 1.

          The electron-emitting device illustrated in  
Fig. 30 comprises a substrate provided thereon with  
insulating layers interposing the face on which fine  
10 particles are dispersed, a stepped portion formed  
between an end portion of the insulating layer and the  
top surface of the substrate, and an electrode  
provided each on the top surface of said insulating  
layer and on the top surface of said substrate; an end  
15 of each electrode being positioned at an upper end or  
lower end of said stepped portion in such a manner  
that said electrode may not come into contact with the  
face on which the fine particles are dispersed; and  
electrode spacing being formed between said electrode  
20 ends, where electrons are emitted by applying a  
voltage between these electrodes.

          In Fig. 30, the numeral 1 and 2 denote  
electrodes for obtaining electrical connection; 4, a  
substrate; 5a, an insulating layer on the substrate 4;  
25 9, fine particles on the insulating layer 5a; 5b, an  
insulating layer to cover the fine particles; and 6,

1 electrode spacing between the electrodes 1 and 2.

In Fig. 30(d), the electron-emitting device of the present invention is a device in which the fine particles 9 interposed between the insulating layers 5a and 5b are arranged at the electrode spacing defined between the electrodes 1 and 2 whose end portions oppose each other (but without overlap) at the stepped portion, and electrons are emitted from the fine particles 9 by applying a voltage between the electrodes 1 and 2.

A preparation method thereof will be described below.

First, the insulating layer 5a is built up or deposited on the substrate by liquid coating, vacuum deposition or the like process, and then the fine particles 9 are dispersed on the insulating layer 5a [see Fig. 30 (a)].

Next, the insulating layer 5b is built up or deposited on the insulating layer 5a and the fine particles 9 by liquid coating or vacuum deposition or the like process so that it may cover the fine particles 9 [see Fig. 30 (b)].

The insulating layers 5a and 5b interposing the fine particles are further formed by photolithoetching so that the stepped portion can be given substantially at the middle of the substrate 4

1 [see Fig. 30 (c)].

Thereafter, the electrodes 1 and 2 are deposited on the insulating layer 5b and the substrate 4 in such a manner that at least part of the sidewall 5 of the stepped portion and the fine particles 9 may not be hidden and also no electric short may be caused, to form the electrode spacing 6 [see Fig. 30 (c)]

The electron-emitting device of the present invention can be obtained according to the above process. The present device may be placed in a vacuum container, a voltage may be applied to the electrodes 1 and 2, and a lead-out electrode plate (not shown) may be disposed so as to face the top surface of the device, to which a high voltage is applied, whereupon electrons are emitted from the vicinity of the electrode spacing 6.

The present invention may still also be embodied for the electron-emitting region 3 by forming an electron-emitting layer 3a and electron-emitting bodies 3b.

For example, as illustrated also in Fig. 31, this is an electron-emitting device having the structure that, for example, the embodiments of Fig. 3 and Fig. 5 previously described are combined.

In Fig. 31, the electron-emitting device of

1 the present invention is a device comprising a  
laminate comprising an insulating layer 5 held between  
a pair of electrodes whose end portions oppose each  
other, wherein the electron-emitting layer 3a is  
5 included into the insulating layer 5 in such a manner  
that the sidewall face of the electron-emitting layer  
3 a may be disposed along the sidewall face of the  
insulating layer 5 formed at the opposing portion at  
which the electrodes 1 and 2 oppose each other, and  
10 the electron-emitting bodies 3b are further disposed  
at the surface of said sidewall, where electrons are  
emitted by applying a voltage between the electrodes 1  
and 2.

The materials and methods for forming the  
15 device are as described previously.

Besides taking the structure as illustrated in  
Fig. 31 to form the electron-emitting region 3, it is  
also desirable to, as shown in Fig. 33, form a stepped  
portion 18 with an insulating layer 5 containing fine  
20 particles (electron-emitting materials) 9 and at the  
same time provide electron-emitting bodies 3b on the  
side surface of said stepped portion.

Alternatively, as shown in Fig. 35, fine  
particles (electron-emitting materials) 9 may be  
25 arranged on an insulating layer 5a, the fine particles  
are further covered thereon with an insulating layer

1 5b to form a stepped portion, and electron-emitting  
bodies 3b may be further arranged on the side surface  
of said stepped portion to form an electron-emitting  
region.

5 In the present invention, the device may also  
comprise an electron-emitting region obtained by three  
or more of its formation methods as shown in Fig. 36.

Incidentally, in the case where the fine  
particles are used as the electron-emitting bodies 3b  
10 dispersed on the side surface or the electron-emitting  
materials 9 contained in the insulating layer as  
described above, it was confirmed that employment of  
two or more kinds of different materials as said fine  
particles enables better control of the  
15 characteristics as the electron-emitting device.

Usable as materials for the fine particles are  
the materials same as those described in relation to  
Fig. 8. Selecting appropriately two or more kinds of  
different materials among those materials as occasion  
20 demands and using them as the fine particles makes it  
possible to not only achieve electron emission but  
also improve or control the characteristics of  
intended electron-emitting devices.

For example, since in the electron-emitting  
25 device of the present invention an electric current in  
the direction of electrodes is indispensable for

1 electron emission, it is possible to lower the drive  
voltage of the device by incorporating fine particles  
of relatively low resistance nature (for example,  
incorporating Pd or Pt fine particles in  $\text{SnO}_2$  fine  
5 particles).

It can be also expected to increase electron  
emission by adding to Pd fine particles, low work  
function materials as exemplified by  $\text{LaB}_6$  or materials  
having a large coefficient of secondary electron  
10 emission as exemplified by an AgMg alloy.

The present invention can be also effective  
not only for the embodiment using the fine particles  
of two or more of different materials, but also for  
the instance where the fine particles, even though  
15 comprised of one kind of materials, are constituted of  
two or more kinds having difference only in physical  
parameters such as average particle diameter and  
shapes.

For example, the particle diameter may be made  
20 to comprise two kinds, one of which is so fine (as  
exemplified by a particle diameter of about 100  
angstroms) that the effect of electric field emission  
can be greatly exhibited, and the other of which is  
relatively so large (as exemplified by a particle  
25 diameter of about 4,000 angstroms) as to be  
contributory only to electrical conductivity, so that

1 the former can realize increase in the amount of  
electron emission, and the latter, driving with a low  
voltage.

It is of course also possible to utilize the  
5 materials by making combination both of the above-  
described two or more kinds of different materials and  
two or more kinds having difference in physical  
parameters as in particle diameter.

To form the fine particles by dispersion, most  
10 simple and convenient is a method in which a  
dispersion of fine particles comprising desired  
materials is coated on a substrate or the like by  
rotary coating, dipping or the like technique,  
followed by heating to remove a solvent, a binder and  
15 so forth. In this instance, adjusting the particle  
diameter of fine particles, content thereof, coating  
conditions, etc, enables control of the state of  
distribution of their dispersion.

There is no established theory as to the  
20 mechanism by which the electrons are emitted from the  
electron-emitting device according to the present  
invention, but it is presumed to be nearly as follows:

Presumed are the electric field emission  
because of the voltage applied to a narrow insulating  
25 layer gap, or the secondary electron emission  
occurring when the electrons emitted from electron-



1 emitting materials are diffracted or scattered by the  
film of the island-like structure or the electrodes,  
or caused by collision, or the thermionic emission,  
hopping electrons, Auger effect, etc.

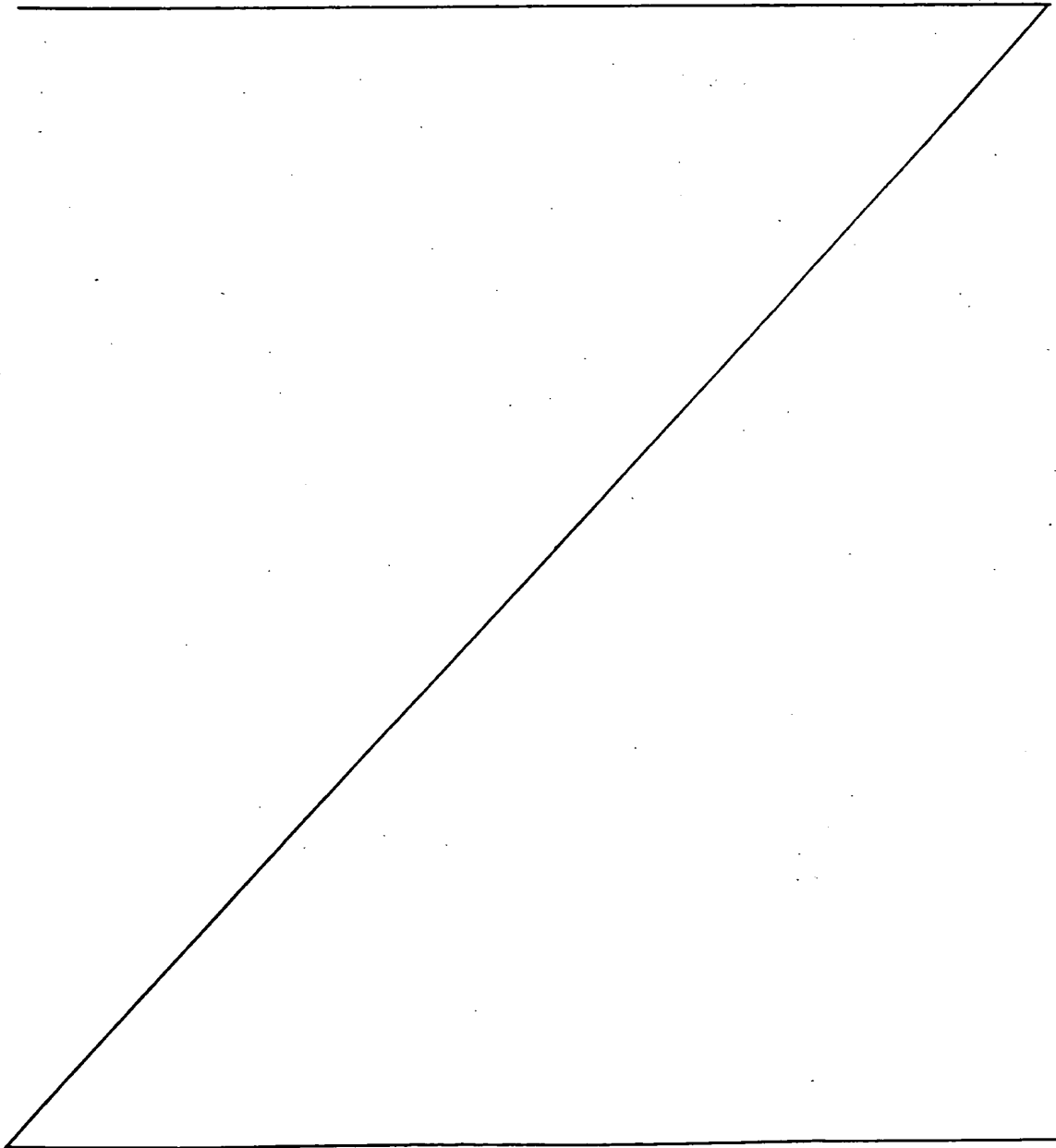
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1 EXAMPLES

Specific examples of the present invention will be described below.

Example 1

5 Fig. 3 (a), (b) is a flow sheet illustrating an example for a method of preparing the electron-emitting device of the present invention.

In Fig. 3 (a), (b), the numeral 4 denotes a glass substrate; and 1, a nickel electrode of 500  
10 angstroms thick.

$\text{SiO}_2$  was vapor deposited to form an insulating layer 5a of 1,000 angstroms thick, Au was vapor deposited as an electron-emitting layer 3a to have a thickness of 500 angstroms, and an insulating layer 5b  
15 was also formed in the same manner as for 5a, thus bringing these three layers into lamination.

Then these were partly laminated on the electrode 1 as illustrated in Fig. 3 (a), along the pattern of the electrode 1, followed by patterning.  
20 Next, Ni was laminated as an electrode 2 with a film thickness of 5,000 angstroms.

As illustrated in Fig. 3 (b), the electrode 2 was subjected to patterning by usual photolithographic process along the patterns of the electrode 1,  
25 insulating layer 5a, electron-emitting layer 3a and insulating layer 5b. As illustrated in the figure,

58

1 the electrodes 2a and 2b were electrically separated,  
and here the area at which the electrode 2b and  
electrode 1 overlap was made as small as possible.

Applying a voltage of 20 V between the  
5 electrode 2a and 2b, there was obtained emission of an  
electron beam of 0.3  $\mu$ A per 1 mm length of width of  
the electrode 2a in the direction vertical to the  
paper surface.

As to the electron-emitting layer 3a, usually  
10 it may show an island structure similar to the small  
island structure among narrow cracks in the  
conventional film prepared by forming, if its film  
thickness is 100 angstroms or less. However, it is  
presumed that even if the film thickness increases to  
15 give a continuous film, the electrodes 1 and 2b are  
electrically insulated, and thus the layer acts  
similarly to the island structure.

#### Example 2

✓ In Fig. 4, the numerals 1 to 5 denotes the  
20 same as in Fig. 3. In this figure, the numeral 8  
denotes an intermediate layer, which is interposed  
between the insulating layer 5b and electrode 2 to  
constitute a multi-layer electrode. In the present  
Example, subsequent to the formation of the insulating  
25 layer 5b, a step to vapor-deposit  $\text{LaB}_6$  to a thickness  
of 1,000 angstroms followed by patterning was added to

1 the preparation steps in Example 1. The electrode 2  
was also formed by using Ni with a thickness of 5,000  
angstroms as in Example 1.

Applying a voltage of 20 V between the  
5 electrode 2a and 2b of the device thus obtained, there  
was obtained emission of an electron beam 7 of 0.5  $\mu$ A  
per 1 mm length of width of the electrode 2a in the  
direction vertical to the paper surface.

### Example 3

10 Fig. 6 (a), (b) is a flow sheet illustrating  
an example for a method of preparing the electron-  
emitting device according to the second embodiment of  
the present invention. In Fig. 6 (a), (b), the  
numeral 4 denotes a glass substrate.

15 An insulating layer 5a was formed with  $\text{SiO}_2$  in  
1,500 angstrom thickness; an electron-emitting layer  
3a, with Pd in 250 angstrom thickness; and an  
insulating layer 5b, with  $\text{SiO}_2$  in 500 angstrom  
thickness, each of which layer was obtained by vacuum  
20 deposition and thereafter, as illustrated in Fig. 6  
(a), etched to have a stepped shape to effect  
patterning. Next, electrodes 1 and 2 are deposited.  
The electrodes are, as illustrated in fig. 6 (b), are  
deposited on the insulating layer 5a and 5b and the  
25 stepped portion formed by the electron-emitting layer  
3a with use of Ni with a thickness of 1,000 angstroms.

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1 In this occasion, generally the electrode 1 will not  
come into contact with the electron-emitting layer 3  
if the thickness of the electrode is made smaller than  
the height of the stepped portion of the insulating  
5 layer 5a, i.e., the step coverage is made poor, and  
also the electrode spacing 6 can be made narrower if  
the insulating layer 5b is made thinner.

The electron-emitting device obtained  
according to the above process was placed in vacuum, a  
10 voltage of 1 kV was applied using a lead-out electrode  
(not shown) provided at an upper area in the drawing,  
and a direct current voltage of about 12 V was applied  
between the electrodes 1 and 2, resulting in emission  
of electrons from the electron-emitting region 3.

15 Example 4

(See Fig. 2.) On a glass substrate 4, an  
insulating layer 5 was deposited using  $\text{SiO}_2$  to a  
thickness of 2,000 angstroms. This was etched to have  
a stepped shape to effect patterning. Next,  
20 electrodes 1 and 2 were deposited with Ni in 1,000  
angstroms thickness by vacuum deposition with masking  
to desired shapes. Here, the step coverage by vapor  
deposited Ni at the stepped portion was generally made  
poor, and the electrode spacing 6 was formed in a  
25 space of about 1,000 angstroms. Fine particles were  
made to be fixed here as electron-emitting bodies 3b.

61

1 The fine particles are obtained, for example, by the  
following manner. Namely, prepared is a solution of  
fine particles of metals such as Pd, having a particle  
diameter of several 100 angstroms as materials serving  
5 as the electron-emitting bodies 3b. This solution was  
coated by spin coating, and baked at a temperature of  
about 300°C to fix the fine particles to the electrode  
spacing region. The resulting device was able to emit  
electrons by driving it as in Example 3.

10           Example 5

In the constitution in Fig. 8, formed on a  
soda lime glass substrate 4 was an insulating layer 11  
comprised of a lead oxide type low-melting glass  
coating film.

15           Pt electrodes 1 and 2 were further formed  
thereon with a thickness of 1,000 angstroms,  $L = 0.5$   
 $\mu\text{m}$  and  $W = 300 \mu\text{m}$ , and Pd, as fine particles 9, of  
several hundred angstroms in particle diameter were  
further arranged in a dispersed state between said  
20 electrodes.

The Pd fine particles 9 were arranged by spin  
coating (3,000 rpm; coating was repeated five times),  
using a butyl acetate solution (Catapaste CCP-4230,  
available from Okuno Seiyaku Kogyo) containing an

1 organic palladium compound in an amount of about 0.3 %  
in terms of Pd metal, and treated by heating at 250°C.  
They were then baked for 20 minutes at 450°C to bring  
the fine particles to be included into the insulating  
5 layer 11.

Here, the amount of an electric current  
flowing to the electrode spacing L was about 5  $\mu$ A/5V.  
This specimen was subjected to pickling using an  
aqueous 5 to 10 vol.% HCl solution, resulting in the  
10 amount of electric current of 250  $\mu$ A/5V.

The specimen prepared according to the above  
process was placed under vacuum of  $10^{-5}$  Torr or more,  
and a voltage was applied between the electrodes 1 and  
2 as described above. As a result, an electric  
15 current  $V_f$  flowed on the surface of inside of the  
insulating layer 11 or through the fine particles 9,  
and a stable electron emission was confirmed when a  
voltage was applied allowing an lead-out electrode  
(not shown) to serve as the anode. The electron  
20 emission was also confirmed in regard to a specimen to  
which no pickling was applied.

Results of measurement on the electron-  
emitting device prepared in the present Example are  
shown in Table 1. Swing of the emitted electric  
25 current is indicated with a value obtained by dividing

1 the amount of change  $\Delta I_e$  in the amount of the emitted electric current of  $1 \times 10^{-3}$  Hz or less by the emitted electric current  $I_e$  and multiplying it by 100, i.e.,  $\Delta I_e / I_e \times 100$ .

5

Table 1

	$V_f$	$I_e$	Efficiency (Emitted current $I_e$ / Device current $I_f$ )	Life*	Swing of emitted current
10	Device drive voltage	Emitted current	Device current $I_f$ )		
<hr/>					
	Present				
15	Example:	$\mu A$			
	30 V	0.8	$8 \times 10^{-3}$	100 hrs	10 %
or more					

\* Life: The period in which the emitted electric current comes to 50 % or less.

20

The above results, as compared with the results of measurement of a surface conduction electron-emitting device comprised of ITO materials that required the forming the conventional technique (drive voltage of the device: 20 V; emitted electric current: 1.2  $\mu A$ ; efficiency:  $5 \times 10^{-3}$ , life: 35 hours; swing of emitted electric current: 20 to 60 %), can

64



1 tell the following:

The electron-emitting device of the present Example is stable and of long life, and shows high characteristics in the electron-emitting efficiency.

5           Example 6

Example 5 was exactly repeated except that the baking for 20 minutes at 450°C was replaced by complete baking for 2 hours at 490°C, to carry out an experiment.

10           The device obtained by the above experiment gives a device in which all the fine particles 9 are penetrated into the insulating layer 11 (Fig. 9).

The same measurement as in Example 5 was made on this electron-emitting device to obtain the same  
15 electron emission as in Example 5, but it tended to have a longer life and show further decreased swing of the emitted electric current.

More specifically, the electron-emitting device in which the fine particles are included into  
20 the insulating layer as in the present Example 6 is characterized by being more improved in the life and the swing of emitted electric current in addition to the effect obtainable in Example 5.

1           Example 7

Example 5 was exactly repeated except that the baking for 20 minutes at 450°C was replaced by baking for 10 minutes at 420°C.

5           The device obtained by the above experiment gives a device as shown in Fig. 10. The electron-emitting device in which the fine particles are slightly penetrated into the insulating layer brought about an electron-emitting device having more improved  
10 emitted electric current and emitted current efficiency ( $I_e/I_f$ ) in addition to the effect obtainable in Example 4.

Example 8

The surface of the insulating layer 11 at the  
15 electrode spacing L of the electron-emitting device obtained in Example 6 was etched using an aqueous 5 Vol.% Hf solution to bring the fine particles 9 to expose from the insulating layer 11, so that there was obtained a device having the same structure as in the  
20 above Example 7.

Example 9

Using a substrate 12 comprising porous glass having a pore size of 80 to 1,000 angstroms in which gold fine particles were deposited to have a device  
25 resistance of from 1 megaohm to 10 megaohms, there was given an electron-emitting device of the present

66

1 invention (Fig. 9).

Measurement on said device was carried out in the same manner as in Example 5. Results are shown in Table 2.

5

Table 2

10	$V_f$	$I_e$	Efficiency	
	Device	Emitted	(Emitted	
	drive	current	current $I_e$ /	Life*
	voltage	current	Device	
			current $I_f$ )	
Present				
15	Example:	$\mu A$		
	25 V	1.0	$2 \times 10^{-3}$	1,000 hrs
				or more

\* Life: The period in which the emitted electric current comes to 50 % or less.

20

It was revealed from the above results that the electron-emitting device of the present invention becomes an electron-emitting device that is stable (i.e. small in the swing of the emitted electric current) and of long life and has a high electron emission efficiency as compared with a conventional

67

1 device obtained by forming of gold (device drive  
voltage of: 16 V; emitted current: 0.8  $\mu$ A; efficiency:  
1.2 x 10<sup>-5</sup>; life: 35 hours; swing: 20 to 60 %). After  
the experiment for electron emission, the degree of  
5 device deterioration was observed by using a scanning  
type electron microscope, but there was seen little  
change in the diameter or distribution of the fine  
particles of gold present between the electrodes.  
However, the device obtained by forming of gold showed  
10 an extreme deterioration at the high resistance part  
discussed in the prior art.

✓ The device according to the present Example 9  
was able to be readily intergrated with less  
irregularities between devices even when a number of  
15 the devices were formed on the same substrate.

#### Example 10

Referring to Fig. 16, obtained was an electron-  
emitting device comprising a colored glass (golden red  
glass) substrate 14 having gold colloids.

20 The same measurement as in Example 5 was made  
on said electron-emitting device. Results obtained  
are shown in Table 3.

1

Table 3

	$V_f$	$I_e$	Efficiency (Emitted current $I_e$ / Device current $I_f$ )	Life*
5	Device drive voltage	Emitted current	Device current $I_f$ )	
<hr/>				
	Present			
0	Example:	$\mu A$		
	32 V	0.6	$2 \times 10^{-2}$	2,000 hrs or more
<hr/>				

\* Life: The period in which the emitted electric current comes to 50 % or less.

15 As will be seen also from Table 3, the electron-emitting device of the present Example is stable (i.e. small in the swing of the emitted electric current) and of long life and has a high electron emission efficiency. After the experiment  
20 for electron emission, the degree of device deterioration was also confirmed by using a scanning type electron microscope, but there was seen little change in the diameter or distribution of the fine particles of gold present between the electrodes. In  
25 contrast therewith, the conventional device obtained by forming of ITO shows an extreme deterioration at

1 the high resistance part.

There was also obtained similar results in the case when, after fine particles are deposited in the glass, the substrate surface was treated with an aqueous hydrofluoric acid solution so that metal colloids may be protruded in a large number from the surface of the glass substrate, thus giving an electron-emitting device of the present invention.

Example 11

10 On a clean, quartz glass substrate of about 1 mm thick, a solution prepared by mixing an organic solvent (Catapaste CCP, available from Okuno Seiyaku Kogyo) containing an organic palladium compound with a  $\text{SiO}_2$  liquid coating preparation (OCD, available from Tokyo Ohka Kogyo) to have a molar ratio of  $\text{SiO}_2$  : Pd of about 5 : 1 was spin-coated with a spinner. Thereafter the resulting coating was baked for 1 hour at about  $400^\circ\text{C}$  to obtain a  $\text{SiO}_2$  insulating layer 11 having a film thickness of about 1,000 angstroms and 15 containing Pd fine particles 9. After this step, the surface of the insulating layer 11 was etched using an aqueous hydrofluoric acid to bring the fine particles 9 to protrude from the insulating layer 11.

Next, on the  $\text{SiO}_2$  insulating layer 11, a photoresist was formed by photolithography with a 25 thickness of about  $0.8 \mu\text{m}$  in the shape giving an

70

1 electrode spacing  $L$ . Further on the  $\text{SiO}_2$  insulating  
layer 11 and said photoresist, a Ni thin film was  
deposited with a thickness of 1,000 angstroms  
according to the masking EB vacuum deposition that  
5 obtains shapes of electrodes. Thereafter the  
photoresist was peeled to carry out a lift-off step to  
remove unnecessary Ni thin film on the photoresist.  
Thus the shapes of the electrodes 1 and 2 and  
electrode spacing  $L$  as shown in Fig. 8 can be formed.  
10 In this instance, each dimension shown in Fig. 8 was  
set to be  $L = 0.1 \mu\text{m}$ ,  $W = 300 \mu\text{m}$  and  $A = 2 \text{ mm}$ .

Electron emission characteristics of the  
electron-emitting device obtained according to the  
above process were measured to have revealed that  
15 there was obtained electron emission of,  
approximately, emitted electric current  $I_e = 1 \mu\text{A}$  and  
emission efficiency  $\alpha = 5 \times 10^{-3}$  under the drive  
voltage  $V_f = 30 \text{ V}$  of the device. The life and the  
swing of the emitted electric current were in  
20 substantially the same level as those in Example 5.

#### Example 12

Example 11 was repeated but replacing the  
organic palladium compound by  $\text{SnO}_2$  fine particles of  
100 angstroms in average particle diameter, to obtain  
25 a similar electron-emitting device, and similar  
experiments were carried out. As a result there was

1 obtained electron emission of substantially the same  
level as in Example 11.

Example 13

In the constitution as illustrated in Fig. 17,  
5 a semiconductor layer 16 of about 100 angstroms thick  
was formed on a soda glass substrate 4 by using a  
carbon film obtained from a calcined organic  
substance. Palladium fine particles of about 100  
angstroms in diameter are dispersed in the  
10 semiconductor layer.

Electrodes 1 and 2 were also formed with Pt to  
have a thickness of 1,000 angstroms, a spacing of 0.8  
 $\mu\text{m}$ , and a width of 300  $\mu\text{m}$ .

Applying a voltage between the electrodes 1  
15 and 2 prepared in the above produced a flow of an  
electric current  $I_f$  through the semiconductor layer 16  
and fine particles 19, and a stable electron emission  
was confirmed when a voltage was applied allowing an  
lead-out electrode to serve as the anode.

20 Comparison of examples of characteristics were  
made between the electron-emitting device prepared in  
the present Example, having a semiconductor, and a  
prior art surface conduction electron-emitting device  
comprised of ITO and requiring the forming, to obtain  
25 the results shown in Table 4. Swing of the emitted  
electric current is indicated with a value obtained by



1 dividing the amount of change  $\Delta I_e$  in the amount of the  
emitted electric current of  $1 \times 10^{-3}$  Hz or less by the  
emitted electric current  $I_e$  and multiplying it by 100,  
i.e.,  $\Delta I_e / I_e \times 100$  (%).

5

Table 4

10	$V_f$	$I_e$	Efficiency (Emitted current $I_e$ / Device current $I_f$ )		Swing of emitted current
	Device drive voltage	Emitted current	Device current $I_f$	Life*	
Present					
15	Example:				
	15 V	4 $\mu$ A	$1 \times 10^{-3}$	800 hrs or more	15 %
	Device of forming of ITO:				
20	20 V	1.2 $\mu$ A	$5 \times 10^{-3}$	35 hrs	20 - 60 %

\* Life: The period in which the emitted electric  
current comes to 50 % or less

As will be clear from Table 4, the surface  
25 conduction electron-emitting device of the present  
Example is characterized by being stable and of long

73

1 life, showing a low drive voltage and a large emitted  
electric current.

#### Example 14

In the constitution illustrated in Fig. 22, an  
5 A-Si:H film was deposited on a glass substrate 4 by  
plasma CVD to have a thickness of 2,000 angstroms,  
thus giving a semiconductor layer 16. Electrodes 1  
and 2 were formed with Pt to have a thickness of 1,000  
angstroms, a spacing L of 0.8  $\mu\text{m}$ , and a width W of 300  
10  $\mu\text{m}$ .

Pd, as fine particles 9, of several 100  
angstroms in diameter were further arranged in a  
dispersed state between said electrodes.

The Pd fine particles 9 were arranged by spin  
15 coating (3,000 rpm; coating was repeated five times),  
using a butyl acetate solution (Catapaste CCP-4230,  
available from Okuno Seiyaku Kogyo) containing an  
organic palladium compound in an amount of about 0.3 %  
in terms of Pd metal, and treated by heating at 250°C.  
20 The electron-emitting device prepared in the present  
Example, having a semiconductor, was evaluated in the  
same manner as in Example 13. As a result, it was  
able to obtain similar electron emission.

#### Example 15

25 In the constitution illustrated in Fig. 25,  
electrodes 1 and 2 were formed on a glass substrate 4

74

1 with Pt to have a thickness of 1,000 angstroms, a  
spacing L of 0.8  $\mu\text{m}$ , a width W of 100  $\mu\text{m}$ .

Fine particles were prepared in the same  
manner as in Example 14, and hydrogenated amorphous  
5 silicon was formed as a semiconductor layer 16 by  
plasma CVD to have a thickness of about 500 angstroms.

Thereafter the convexes on the semiconductor  
layer 16 were etched by ion milling.

The electron-emitting device prepared  
10 according to the above process was evaluated in the  
same manner as in Example 12 to have found that there  
is obtained similar electron emission. Particularly  
in the present Example, different from Example 14, the  
electron-emitting device in which the fine particles 9  
15 were fixed in the semiconductor layer 16 had a  
tendency of stableness in electron emission in  
addition to the effect obtainable in Example 14.

#### Example 16

An electron-emitting device was obtained  
20 according to the previously described preparation  
steps (a) to (c) of Fig. 28.

More specifically, on a clean, quartz glass  
substrate of about 1 mm thick, a solution prepared by  
mixing an organic solvent (Catapaste CCP, available  
25 from Okuno Seiyaku Kogyo) containing an organic

1 palladium compound with a  $\text{SiO}_2$  liquid coating  
preparation (OCD, available from Tokyo Ohka Kogyo) to  
have a molar ratio of  $\text{SiO}_2$  : Pd of about 5 : 1 was  
spin coated with a spinner. Thereafter the resulting  
5 coating was baked for 1 hour at about  $400^\circ\text{C}$  to obtain  
a  $\text{SiO}_2$  insulating layer 5 having a film thickness of  
about 1,500 angstroms and containing Pd fine particles  
9 [see Fig. 28 (a)].

Next, the insulating layer 5 was etched by  
10 photolithoetching with use of an aqueous hydrofluoric  
acid solution to form a stepped portion of about 1,500  
angstroms high at the middle of the substrate 4 [see  
Fig. 28 (b)].

Thereafter, Ni electrodes 1 and 2 of about 500  
15 angstroms in film thickness was formed by deposition  
utilizing EB vacuum deposition in the manner that the  
stepped portion may not be completely covered.

In this instance, there is given the structure  
that the electrodes 1 and 2 oppose each other with  
20 certain spacing, across the side wall of the stepped  
portion of the insulating layer 5 containing the fine  
particles 9. This space is designated as electrode  
spacing 6 [see Fig. 28 (c)].

Electron emission characteristics of the  
25 electron-emitting device obtained according to the  
above process were measured to have revealed that

1 there was obtained electron emission of,  
approximately, emitted electric current  $I_e = 2.5 \mu A$   
and emission efficiency  $\alpha = 5 \times 10^{-3}$ .

Example 17

5 According to the previously described  
preparation steps (a) to (c) of Fig. 29, prepared was  
an electron-emitting device of the constitution that  
an insulating layer is held between electrodes.

More specifically, on a clean, quartz glass  
10 substrate 4 of about 1 mm thick, an Ni electrode of  
about 500 angstroms in film thickness was deposited by  
EB vacuum deposition to form an electrode 1 by  
photolithoetching [see Fig. 29 (a)].

Next, on the surface of the electrode 1 and  
15 the substrate 4, a  $SiO_2$  insulating layer 5 containing  
Pd fine particles 9 was deposited in the same manner  
as in Example 16 to have a film thickness of about  
1,000 angstroms. A Ni thin film of about 1,000  
angstroms in film thickness was further deposited on  
20 the  $SiO_2$  insulating layer to give an electrode  
material 2c [see Fig. 29 (b)].

Thereafter, on the Ni thin film, formed was a  
photoresist in the shape of an electrode 2 partly  
overlapping with the electrode 1 at the middle of the  
25 substrate. In the shape of this photoresist, the  
electrode material 2c and insulating layer 5 were

77

1 etched, followed by peeling of the resist to form the  
electrode 2 and an electrode spacing 6. The size  
other than thickness, of each material, was made to be  
the same as in Example 16.

5            Electron emission characteristics of the  
electron-emitting device obtained according to the  
above process were measured. As a result, there was  
obtained the same electron emission as in Example 16.

Example 18

10           Example 16 was repeated except that the  
material for fine particles and the organic solvent  
comprising the organic metal compound were replaced by  
a  $\text{SiO}_2$  liquid coating preparation in which  $\text{SnO}_2$  fine  
particles of about 100 angstroms in primary particle  
15 diameter were dispersed, to carry out an experiment.  
As a result, there was obtained the same electron  
emission as in Example 16.

Example 19

20           An electron-emitting device was obtained  
according to the previously described preparation  
steps (a) to (d) of Fig. 30.

More specifically, on a clean, quartz glass  
substrate of about 1 mm thick, a  $\text{SiO}_2$  liquid coating  
preparation (Catapaste CCP, available from Okuno  
25 Seiyaku Kogyo) was spin-coated with a spinner.

74

1 Thereafter the coating was baked for 1 hour at about  
400°C to obtain an insulating layer 5a comprised of  
SiO<sub>2</sub> and having a film thickness of about 1,000  
angstroms. Subsequently, on the insulating layer 5a,  
5 an organic solvent (Catapaste CCP, available from  
Okuno Seiyaku Kogyo) containing an organic palladium  
compound was spin coated with a spinner. Thereafter  
the coating was baked for 10 minutes at about 250°C to  
obtain fine particles 9 comprised of Pd in the state  
10 that they are dispersed on the surface of the  
insulating layer 5a [see Fig. 30 (a)].

Next, on the fine particles 9 and insulating  
layer 5a, an insulating layer 5b comprised of SiO<sub>2</sub> was  
coated in the same manner as the insulating layer 5a  
15 to have a film thickness of about 500 angstroms,  
followed by baking [see Fig. 30 (b)].

Thereafter, the insulating layers 5a and 5b  
were etched using an aqueous hydrofluoric acid  
solution by photolithoetching to form a stepped  
20 portion of about 1,500 angstroms high at the middle of  
the substrate 4 [see Fig. 30 (c)].

Ni electrodes 1 and 2 of about 5,000 angstroms  
in film thickness was further formed by deposition  
utilizing EB vacuum deposition in the manner that the  
25 stepped portion may not be completely covered. A  
space thus formed is designated as electrode spacing 6

1 [see Fig. 30 (d)].

Electron emission characteristics of the electron-emitting device obtained according to the above process were measured to have revealed that  
5 there was obtained electron emission of, approximately, emitted electric current  $I_e = 2.0 \mu A$  and emission efficiency  $\alpha = 8 \times 10^{-3}$ .

Example 20

As illustrated in Fig. 32, a Ni electrode 1 of  
10 500 angstroms thick was formed on a glass substrate 4 by vacuum deposition. On the electrode 1, an insulating layer 5a made of  $SiO_2$  was formed by vacuum deposition utilizing sputtering to have a film thickness of 1,000 angstroms.

15 Next, an electron-emitting layer made of Au was formed in 500 angstroms thickness by vacuum deposition (a layer 3a), and thereafter an insulating layer 5b ( $SiO_2$ ) was formed with a film thickness of 1,000 angstroms by sputtering.

20 After the respective layers of the insulating layer 5a, electron-emitting layer 3a and insulating layer 5b were laminated, they are partly laminated on the electrode 1 as illustrated in Fig. 32 (a) along the pattern of the electrode 1, followed by  
25 patterning. Next, an electrode 2 is laminated. The electrode 2 was made of Ni to make wiring resistance



1 lower. The thickness thereof was controlled to 5,000 angstroms to obtain necessary wiring resistance.

After the electrode 2 was laminated by vacuum deposition, the electrode 2 was subjected to  
5 patterning by, for example, usual photolithographic process along the patterns of the electrode 1, insulating layer 5a, electron-emitting layer 3a and insulating layer 5b as illustrated in Fig. 32 (b).

A Pd organic metal solution (Catapaste,  
10 available from Okuno Seiyaku Kogyo Co.) was spin coated as an electron-emitting layer, followed by baking for 10 minutes at 250°C to provide electron-emitting bodies on the surface of a side wall of the insulating layers. A voltage of 14 V was applied  
15 between the electrodes 2a and 2b using a lead-out electrode (not shown) provided above the device substrate, and a lead-out voltage of 500 V was applied to obtain emission of electron beams 7 of 1.7  $\mu$ A.

#### Example 21

20 ✓ Fig. 33 (d) illustrate a cross section of a electron-emitting device obtained in the present Example [See Fig. 33 (a) to (d) as to the preparation steps].

On a clean, quartz glass substrate 4 of about  
25 1 mm thick, a solution prepared by mixing an organic palladium compound solution (Catapaste CCP, available

1 from Okuno Seiyaku Kogyo) with a  $\text{SiO}_2$  liquid coating  
preparation (OCD, available from Tokyo Ohka Kogyo) to  
have a molar ratio of  $\text{SiO}_2$  : Pd of about 10 : 1 was  
spin coated with a spinner. Thereafter the resulting  
5 coating was baked for 1 hour at about  $400^\circ\text{C}$  to obtain  
a  $\text{SiO}_2$  insulating layer 5 having a film thickness of  
about 3,500 angstroms and containing electron-emitting  
materials 9 (Pd fine particles) [see Fig. 33 (a)].

Next, the insulating layer 5 was etched by  
10 photolithoetching with use of an aqueous hydrofluoric  
acid solution to form a stepped portion 18 of about  
3,500 angstroms high at the middle of the substrate 4  
[see Fig. 33 (b)].

Thereafter, Ni electrodes 1 and 2 of about 500  
15 angstroms in film thickness was formed by deposition  
utilizing EB vacuum deposition to have the shape  
illustrated in Fig. 33 (c) in the manner that the  
stepped portion may not be completely covered.

Electron emitting bodies 3b were further  
20 provided on the surface of a side wall of the  
insulating layer in the same manner as in Example 19  
[see Fig. 33 (d)].

Electron emission characteristics of the  
electron-emitting device obtained according to the  
25 above process were measured to have revealed that  
there was obtained electron emission of,

1 approximately, emitted electric current  $I_e = 4 \mu\text{A}$  and  
emission efficiency  $\alpha = 2 \times 10^{-3}$ , under applied device  
voltage  $V_f = 14 \text{ V}$  and lead-out voltage  $V_a = 1 \text{ kV}$ .

Example 22

5           Example 21 was repeated except that the  
organic metal compound solution that formed the  
electron-emitting bodies 3b in Example 21 was replaced  
by a  $\text{SiO}_2$  liquid coating preparation in which  $\text{SiO}_2$   
fine particles of about 100 angstroms in particle  
10 diameter were dispersed, to form a similar electron-  
emitting device. There were obtained substantially  
the same results as in Example 21.

Example 23

Similar results were obtained also when the  
15 organic metal compound solution employed to form the  
electron-emitting bodies 3b in Example 20 was replaced  
by a coating preparation in which  $\text{SnO}_2$  fine particles  
of about 100 angstroms in particle diameter were  
dissolved by dispersion together with an organic  
20 binder.

Example 24

On a substrate a  $\text{SiO}_2$  film is vacuum deposited  
to form an insulating layer 5a, on which Pd is vacuum  
deposited in a thickness of 500 angstroms (electron-  
25 emitting layer 3a) and further an insulating layer 5b

1 is formed by vacuum deposition of a  $\text{SiO}_2$  film [see Fig. 34 (a)].

Next, the insulating layers 5a, 5b and electron-emitting layer 3a are etched to form a stepped portion 18 [see Fig. 34 (b)].

Thereafter, Ni is applied by masking vacuum deposition in a thickness of 500 angstroms to form electrodes 1 and 2 [see Fig. 34 (c)].

An organic palladium solution is further coated on the surface of the device substrate, followed by baking to provide electron-emitting bodies 3b on the sidewall of the stepped portion [see Fig. 34 (d)].

The resulting electron-emitting device has the structure that electron-emitting materials are present only in the vicinity of the stepped portion in contrast with Example 20.

Good results were obtained as in Example 20.

#### Example 25

Example 24 was repeated to obtain an electron-emitting device, except that the Pd fine particles film of the electron-emitting layer 3a in Example 24 was replaced by a layer obtained by coating a Pd fine particles dispersed solution as shown in Fig. 35.

There was obtained the same electron emission.

#### Example 26

1           The same electron emission as in Example 20  
was obtained also in a device in which as illustrated  
in Fig. 36 a Pd vapor-deposited film serving as an  
electron-emitting layer 3a was disposed in an  
5 insulating layer 5 containing electron-emitting  
materials 9 as Pd fine particles, a stepped portion  
was formed, and electron-emitting bodies 3b were  
further provided on the sidewall of the stepped  
portion by coating an organic palladium solution  
10 followed by baking.

Example 27

In the constitution illustrated in Fig. 37, on  
a glass substrate 4, titanium electrodes 1 and 2 were  
formed with a thickness of 1,000 angstroms,  $L = 0.8 \mu m$   
15 and  $W = 300 \mu m$ , and thereafter  $SnO_2$  and Pd were  
arranged as fine particles in a dispersed state  
between the electrodes.

As a method therefor, a  $SnO_2$  dispersion ( $SnO_2$ :  
1g; solvent: MEK (methyl ethyl ketone)/cyclohexanone =  
20 3/1, 1,000 cc; butyral: 1 g) having a primary particle  
diameter of 80 to 200 angstroms was spin-coated,  
followed by heating. A Pd dispersion having a primary  
particle diameter of about 100 angstroms was further  
spin coated, followed by heating to obtain an electron-  
25 emitting device.

A voltage of about  $10^{-5}$  Torr was applied

1 between the electrodes of the device thus formed. As  
a result, there was obtained an electron emission  
current of 1.1  $\mu$ A under an applied voltage of 15 V.

Thus, substantially the same electron emission  
5 is obtained even under the applied voltage of lower by  
approximately 5 volts than that of the device  
containing no Pd fine particles and solely comprised  
of  $\text{SnO}_2$ . In this manner, the drive voltage was able  
to be lowered by the device containing different kind  
10 of fine particles.

Example 28

In regard to the  $\text{SnO}_2$  dispersion of Example  
27, a dispersion of  $\text{SnO}_2$  of 80 to 200 angstroms in  
particle diameter and a dispersion of  $\text{SnO}_2$  of about  
15 3,000 angstroms in particle diameter were prepared,  
and two kinds of the  $\text{SnO}_2$  dispersions were coated in  
the same manner as in Example 27 but in one step for  
each dispersion, thus arranging fine particles in a  
dispersed state to obtain a electron-emitting device.

20 As electron emission characteristics of the  
device thus formed, there was obtained an electron  
emission current of about 1.1  $\mu$ A under an applied  
voltage of 17 V.

Thus, substantially the same electron emission  
25 is obtained even under the applied voltage of as about  
3 V lower than that of the device obtained by coating

1 in two steps the dispersions of  $\text{SnO}_2$  of 80 to 200  
angstroms in particle diameter. In this manner, the  
drive voltage was able to be lowered by adding the  
particles having a larger particle diameter.

5 ~~10~~ [Effect of the invention]

As described above, according to the electron-  
emitting device of the present invention and the  
method for preparing the same, electron-emitting  
devices that can have stable structure even if the  
10 electrode spacing having the electron-emitting  
materials is made very narrow can be formed without  
applying the forming required in the prior art.

Accordingly, the electron-emitting devices  
prepared by the present invention are quite free from  
15 the difficulties conventionally accompanying the  
forming treatment, so that it becomes possible to  
manufacture the devices having less irregularities in  
characteristics, in a large number and with ease,  
bringing about great industrial utility.

20 The electron-emitting device obtained by the  
present invention can also be utilized in planar  
display devices in which the electron-emitting devices  
are mounted in a single plane and electrons emitted by  
applying a voltage are accelerated to stimulate  
25 phosphors to effect light-emission.

An electron-emitting device that is stabler

87

1 and of longer life and also has a good efficiency can  
also be obtained by bringing the electrode  
constitution into a multi-layer constitution.

Also, the electron-emitting device in which  
5 the fine particles are fixed in the insulating layer  
is free of any movement of the fine particles during  
drive, and thus can be an electron-emitting device  
that is stable and of elongated life.

The electron emission efficiency can be  
10 improved by suitably adjusting the density of the fine  
particles.

The electron-emitting device having the  
semiconductor layer as illustrated in Fig. 17 makes it  
possible to lower the drive voltage by controlling the  
15 electrical resistance of the semiconductor, and also  
can be effective in improvement of emitted currents.

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